

Exchange coupling in Eu monochalcogenides from first principles

J. Kuneš,^{1,2} Wei Ku,^{1,*} and W.E. Pickett¹

¹*Department of Physics, University of California, One Shields Avenue, Davis CA 95616, USA[†]*

²*Institute of Physics, Academy of Sciences of the Czech Republic,
Cukrovarnická 10, 162 53 Praha 6, Czech Republic*

(Dated: February 2, 2008)

Using a density functional method with explicit account for strong Coulomb repulsion within the $4f$ shell, we calculate effective exchange parameters and the corresponding ordering temperatures of the (ferro)magnetic insulating Eu monochalcogenides (EuX; X=O,S,Se,Te) at ambient and elevated pressure conditions. Our results provide quantitative account of the many-fold increase of the Curie temperatures with applied pressure and reproduce well the enhancement of the tendency toward ferromagnetic ordering across the series from telluride to oxide, including the crossover from antiferromagnetic to ferromagnetic ordering under pressure in EuTe and EuSe. The first and second neighbor effective exchange are shown to follow different functional dependencies. Finally, model calculations indicate a significant contribution of virtual processes involving the unoccupied f states to the effective exchange.

PACS numbers: 75.50.Pp, 75.30.Et, 71.27.+a

Ferromagnetic semiconductors have become object of a great technological interest with the appearance of spintronics because they can provide a spin-dependent tunneling barrier. Especially challenging is to achieve a sizable ordered moment at room temperature, which is crucial for a large scale application of the technology. The ability to calculate the ordering temperature and understand the exchange mechanisms on the material specific level is of particular importance. There is currently an intense effort to locate such materials within the dilute magnetic semiconductors, where the magnetic moment is carried by impurities in an otherwise non-magnetic system, but few candidates have been found. An attractive alternative is FM insulators. Ferromagnetism is rare in stoichiometric materials without charge carriers. Europium monochalcogenides (EuO, EuS, EuSe, EuTe) belong to this small group of ferromagnetic insulators [1].

Crystallizing in the rock-salt structure, the first two members of the group order ferromagnetically at 69.2 K and 16.6 K respectively [2], while EuTe, a type II antiferromagnet, becomes ferromagnetic only at elevated pressure [3]. EuSe is at the border line between ferromagnetic and antiferromagnetic order with ferromagnetism stabilized by a moderate pressure of 0.5 GPa [4]. Application of pressure strongly enhances Curie temperatures of all these materials. The Eu^{2+} valency results in half filling of the Eu $4f$ shell with 8S configuration of the groundstate multiplet. Due to the localized nature of the moment-carrying f orbitals, inter-site exchange interactions can only be mediated by the valence and conduction electrons. The intra-atomic $f-d$ and $f-s$ exchange, which is the leading f -valence interaction, gives rise to temperature dependent features (red shift effect) in the valence electron spectrum which are well captured by the ferromagnetic Kondo lattice model [5, 6]. It is due to the insulating groundstate that this interaction alone cannot

give rise to an effective coupling between the local moments. To do so excitations across the gap and/or mixing of the f and valence/conduction bands has to be taken into account. The relevant exchange processes have been discussed previously on a qualitative level [7, 8, 9]. While a significant amount of *ab initio* calculations of the Curie temperature in metallic systems has been done (e.g. Ref. 10 and references therein) attempts to address the Curie temperature and coupling mechanisms of ferromagnetic insulators on a first principles level are rare and become quite involved [11, 12].

The f states in rare earths such as Eu pose an extra challenge in obtaining a quantitative microscopic theory. *Ab initio* electronic structure methods based on density functional theory (DFT) [13] and the standard semi-local approximations [14, 15] have notorious problems in dealing with the strong correlations within the $4f$ shell. In particular these approximations often result in incorrect filling of the $4f$ states. Early bandstructure calculation of europium chalcogenides by Cho [16] using empirical potential did not address the inter-site exchange coupling. In this work we use the LDA+U method [17], which provides correct filling of the $4f$ states while allowing for mixing with the rest of the band (unlike the frequently used open-core treatment). Just as importantly, positions of the resulting occupied and unoccupied f bands are realistic. The half filling of the $4f$ shell in Eu^{2+} removes additional problems associated with orbital degrees of freedom.

The calculations reported here were performed using the Wien2k[18] implementation of the full-potential linearized augmented-plane-waves (FLAPW) method with the rotationally invariant LDA+U functional and double-counting scheme of Ref. 17. The size of APW+lo basis was determined by the cut-off $R_{mt}K_{max}=8$ corresponding to approximately 100 basis functions per atom. Ap-

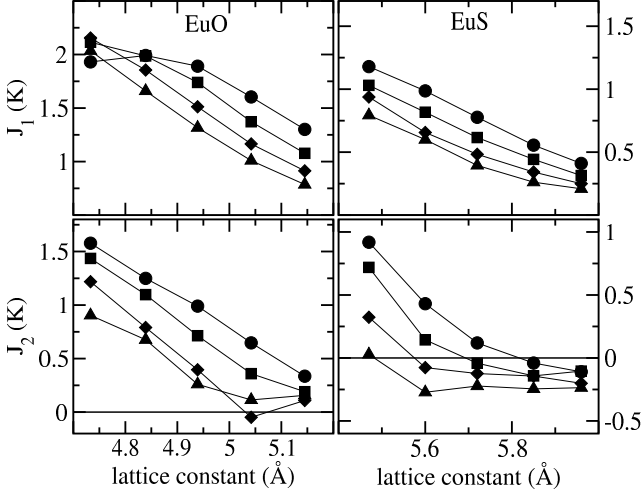


FIG. 1: The nearest-neighbor J_1 and next-nearest-neighbor J_2 effective exchange parameters in EuO and EuS as functions of the lattice constant calculated for different values of U (circle – 6 eV, square – 7 eV, diamond – 8 eV, triangle – 9 eV, the lines serve as guides for eye). The deviation for the linear dependence of J_1 at high pressures for EuO coincides with the onset of metallic behavior due to overlap of the f and valence band.

proximately 30 irreducible k -points (depending on the magnetic structure) out of the 250- k -point regular grid were used in the Brillouin zone integrations. The calculations were performed for lattice constants spanning the experimental range of stability of the rock salt crystal structure. The groundstate energies of three different magnetic structures: (i) ferromagnetic (F), (ii) type II antiferromagnetic and (iii) antiferromagnetic with propagation vector $(0,0,\frac{2\pi}{a})$, were calculated self-consistently and mapped on Heisenberg Hamiltonian

$$H = - \sum_{i,j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \quad (1)$$

with nearest-neighbor J_1 and next-nearest-neighbor J_2 interaction, which is known experimentally to provide a good description of magnetic behavior of the materials in question. The classical energies corresponding to spin configurations (i) to (iii) are $-(12J_1 + 6J_2)S^2$, $6J_2S^2$ and $(4J_1 - 6J_2)S^2$ respectively. The ferromagnetic energies were calculated with the lattices of both antiferromagnetic structures and the corresponding energy differences were taken. The assumption of $J_1 - J_2$ model was checked for EuS at ambient pressure by spin-spiral calculation similar to those of Ref. 19, which yielded dispersion consistent with $J_1 - J_2$ model. The calculated exchange constants as function of lattice parameter for values of U from 6 eV to 9 eV are shown in Fig. 1 and Fig. 2.

From the parameters of the Heisenberg Hamiltonian ordering temperatures were calculated using result of the

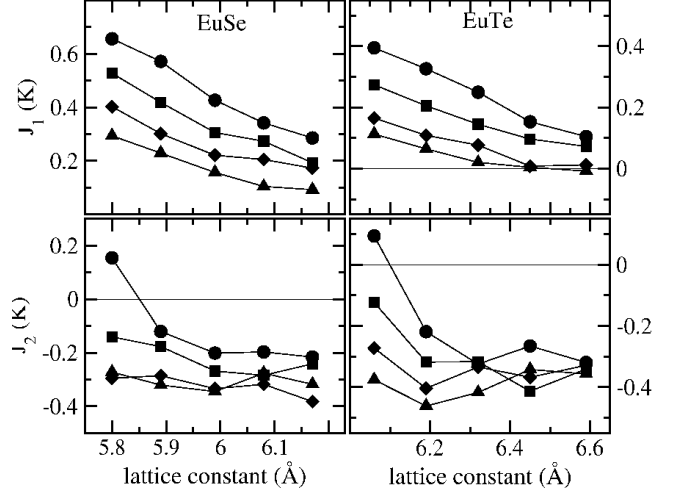


FIG. 2: The same as in Fig. 1 for EuSe and EuTe.

Tyablikov decoupling method [20, 21]

$$(k_B T_C)^{-1} = \frac{2S(S+1)}{3} \frac{1}{N} \sum_{\mathbf{q}} [J(0) - J(\mathbf{q})]^{-1}, \quad (2)$$

where $J(\mathbf{q})$ stands for the lattice Fourier transform of the effective exchange parameter. The alignment in the groundstate is determined by the sign of $J_1 + J_2$ (positive–ferromagnetic, negative–antiferromagnetic). For EuTe we have calculated the Néel temperature as well using generalized equation (2) [22]. The ordering temperatures as functions of lattice constant are shown in Fig. 3 and Fig. 4 and compared to the experimental data of Goncharenko and Mirebeau [23, 24] (see also [3, 4]). The estimated numerical accuracy is about 10 K. The trend of weakening ferromagnetism in favor of antiferromagnetism when going from oxide to telluride is well reproduced and is common to all values of U . The effective exchange is rather sensitive to the value of U , yet the literature value of 6 eV to 7 eV [25] gives the best agreement throughout the series. Both the significant increase of the Curie temperature with pressure and almost constant behavior of the Néel temperature of EuTe at lower pressures observed experimentally are well captured by the calculations

Based on the fact that in the type II antiferromagnetic structure the first neighbor exchange is frustrated and thus the mean-field Néel temperature is proportional to J_2 , Goncharenko and Mirebeau concluded that J_2 is pressure independent while J_1 exhibits a non-linear increase with the applied pressure. In their scenario the transition from low-pressure antiferromagnetic groundstate to high-pressure ferromagnetic groundstate is solely due to the increase of J_1 . Our calculations provide a different picture. With the only exception being EuO at high pressure, we find more or less linear dependence of J_1 on the lattice parameter. On the other hand J_2 exhibits quite

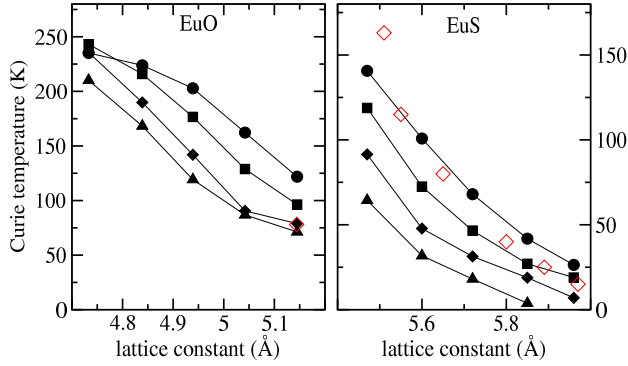


FIG. 3: The magnetic ordering temperatures of EuO and EuS calculated for different values of U (see caption of Fig. 1). The experimental values for EuO [26] and EuS [24] are marked with open diamonds.

non-linear behavior, which in the case of EuTe translates to being almost constant at low pressures and increasing rapidly at higher pressures, which significantly contributes to stabilization of the ferromagnetic state.

The success of the LDA+ U functional in describing the trend across the chalcogenide series as well as capturing the pressure dependence of the ordering temperature indicates that the relevant coupling mechanisms are well accounted for. While we can not identify directly the leading coupling mechanisms we can make several observations connected to the sensitivity of the results to the value of U . The value of U affects inter-site coupling in two distinct ways: (i) through the position of the occupied f bands within the semiconducting gap, which is decisive for hybridization with the valence and conduction bands, (ii) through the splitting between the occupied and unoccupied f bands. In order to stress the importance of including hybridization effects in the f bands we show the spin-majority bandstructure of EuO in Fig. 5. The f band exhibits appreciable dispersion with a bandwidth of about 1 eV which is mostly due to mixing with O $2p$ valence bands. A similar picture is obtained for the other members of the series with the f bands being localized deeper in the gap when going toward telluride.

The intra-atomic $f-s$ or $f-d$ exchange is determined solely by the spin density. The coupling mechanisms involving only the intra-atomic exchange are therefore insensitive to the value of U . The Bloembergen-Rowland (BR) coupling [27], inter-band analog of the Ruderman-Kittel-Kasuya-Yosida (RKKY) coupling well known in metals, is the leading mechanism of this type. A discussion of BR coupling was given earlier by Lee and Liu [9], starting from diagonalized band Hamiltonian and adding interband exchange term, and by Kasuya [7] and Sawatzky *et al.* [8], starting from atomic orbitals with $f-d$ exchange and conduction-valence (Eu $d-Xp$) hybridization. The sizable dependence of our results on

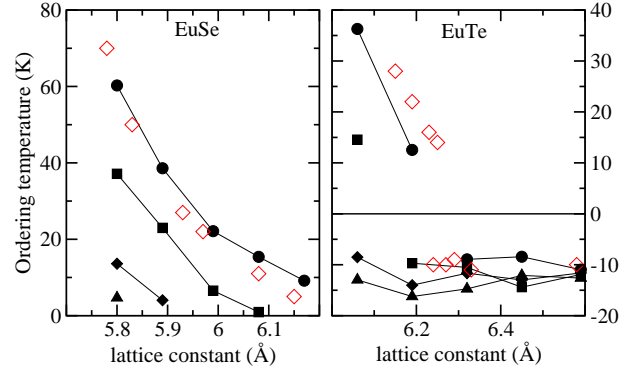


FIG. 4: The magnetic ordering temperature of EuSe and EuTe calculated for different values of U (see caption of Fig. 1). The negative values for EuTe correspond to Néel temperature and antiferromagnetic groundstate. The experimental values marked with open diamonds are taken from Ref. [23].

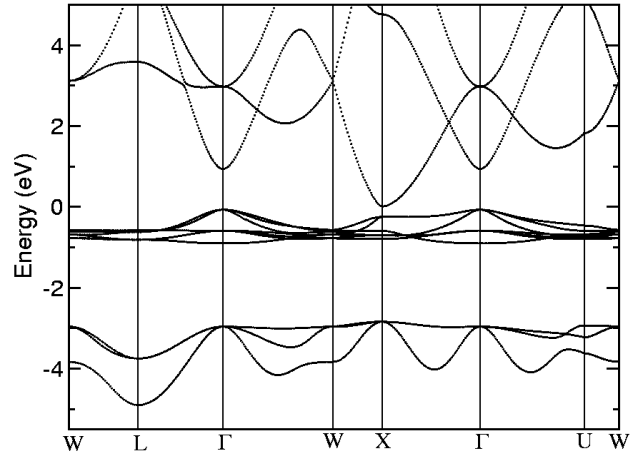


FIG. 5: Majority spin bandstructure of EuO obtained with U of 7 eV at ambient pressure. The valence bands have dominant O $2p$ character while the conduction bands are mostly Eu d and s states.

the value of U indicates that additional mechanisms are involved.

We have performed a simple model calculation to evaluate the role of unoccupied f bands which participate, for example, in the superexchange mechanism. By adding an orbital dependent auxiliary potential, which acts only on the minority-spin f orbitals, we control the ‘site energy’ of the unoccupied (minority-spin) f states without affecting the occupied f ’s. Obviously such a term does not enter the groundstate energy directly, but only through the mixing of the minority-spin f bands with the occupied bands. Excitations from occupied to unoccupied bands correspond to hopping of an f electron from one Eu atom to another, resulting in superexchange interaction. By looking at the dependence of the effective exchange parameters on the splitting of the occupied and unoccupied f bands controlled by the auxiliary potential we can as-

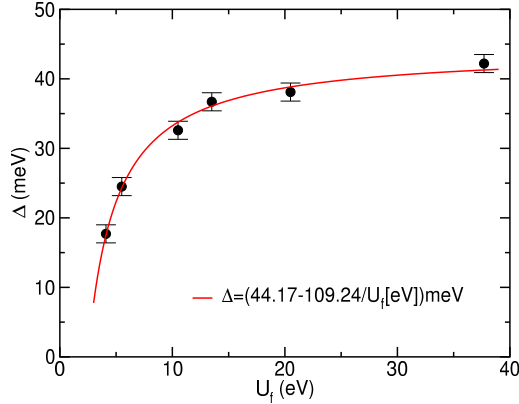


FIG. 6: Difference between the groundstate energies of type II antiferromagnetic and ferromagnetic structures as a function of the splitting U_f between the occupied and unoccupied f bands obtained with auxiliary potential on top of LDA+U with U of 7 eV. U_f of 11 eV corresponds to zero auxiliary potential.

sess the relative importance of the superexchange and virtual processes involving change in the $4f$ occupation in general. In Fig. 6 we show the energy difference between the ferromagnetic and type II antiferromagnetic groundstates as a function of energy separation between the occupied and unoccupied f bands. Apparently the auxiliary potential has a sizable effect consistent with $1/U_f$ dependency of the superexchange interaction.

Now we summarize. Our calculations show that accounting for intra-atomic repulsion using the LDA+U method provides a reliable description of effective exchange coupling in ferromagnetic insulators with localized moments. The trend favoring ferromagnetism for lighter chalcogenides as well as the under-pressure antiferro-to-ferromagnetic transition in EuSe and EuTe are well captured. The pressure dependences of the magnetic ordering temperatures, which correspond well to the experimental observations, are connected to distinct under-pressure behavior of the exchange parameters J_1 and J_2 . The exchange coupling is strongly effected even by the unoccupied f bands establishing the important role of virtual hopping processes between the f shells on neighboring atoms.

This work was supported by NSF Grant DMR-0114818 and by the SSAAP program (DE-FG03-03NA00071) at University of California Davis.

under Contract No. DE-AC02-98 CH 10886.

[†] Electronic address: kunes@fzu.cz

- [1] For review see A. Mauger and C. Godart, Phys. Rep. **141**, 51 (1986).
- [2] L. Passell, O. W. Dietrich, and J. Als-Nielsen, Phys. Rev. B **14**, 4897 (1976).
- [3] M. Ishizuka, Y. Kai, R. Akimoto, M. Kobayashi, K. Amaya, and S. Endo, J. Magn. Magn. Mater. **166**, 211 (1997).
- [4] H. Fujiwara, H. Kadomatsu, M. Kurisu, T. Hihara, K. Kojima, and T. Kamigaichi, Solid State Commun. **42**, 509 (1982).
- [5] R. Schiller, W. Müller, and W. Nolting, Phys. Rev. B **64**, 134409 (2001).
- [6] W. Müller and W. Nolting, Phys. Rev. B **66**, 085205 (2002).
- [7] T. Kasuya, IBM J. Res. Dev. Educ. **14**, 214 (1970).
- [8] G. A. Sawatzky, W. Geertsma, and C. Haas, J. Magn. Magn. Mater. **3**, 37 (1976).
- [9] V.-C. Lee and L. Liu, Phys. Rev. B **30**, 2026 (1984).
- [10] M. Pajda, J. Kudrnovský, I. Turek, V. Drchal, and P. Bruno, Phys. Rev. B **64**, 174402 (2001).
- [11] W. Ku, H. Rosner, W. E. Pickett, and R. T. Scalettar, Phys. Rev. Lett. **89**, 167204 (2002).
- [12] S. Feldkemper, W. Weber, J. Schulenburg, and J. Richter, Phys. Rev. B **52**, 313 (1995).
- [13] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
- [14] W. Kohn and L. Sham, Phys. Rev. **140**, A1133 (1965).
- [15] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992).
- [16] S. J. Cho, Phys. Rev. B **1**, 4589 (1970).
- [17] V. I. Anisimov, I. V. Solovyev, M. A. Korotin, M. T. Czyzyk, and G. A. Sawatzky, Phys. Rev. B **48**, 16929 (1993).
- [18] P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka, and J. Luitz, *WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties* (Karlheinz Schwarz, Techn. Universität Wien, Wien, 2001), ISBN 3-9501031-1-2.
- [19] J. Kuneš and R. Laskowski, cond-mat/0404369.
- [20] S. V. Tyablikov, *Methods of Quantum Magnetism* (Plenum Press, New York, 1967).
- [21] R. A. Tahir-Kheli and D. ter Haar, Phys. Rev. **1962**, 88 (1962).
- [22] I. Turek, J. Kudrnovský, M. Diviš, P. Franek, G. Bihlmayer, and S. Blügel, Phys. Rev. B **68**, 224431 (2003).
- [23] I. N. Goncharenko and I. Mirebeau, Europhys. Lett. **37**, 633 (1997).
- [24] I. N. Goncharenko and I. Mirebeau, Phys. Rev. Lett. **80**, 1082 (1998).
- [25] B. N. Harmon, V. P. Andropov, A. I. L. abd I. V. Solovyev, and V. I. Anisimov, J. Phys. Chem. Solids **56**, 1521 (1995).
- [26] W. Zinn, J. Magn. Magn. Mater. **3**, 23 (1967).
- [27] N. Bloembergen and T. J. Rowland, Phys. Rev. **97**, 1679 (1955).

* current address: Department of Physics, Brookhaven National Laboratory, managed by BSA for U.S. DOE